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Submitted to Analytical Chemistry

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October 1980

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Prepared for the U.S. Department of Energy under Contract W-7405-ENG-48

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PEAK RESOLUTION BY SEMIDERIVATIVE VOLTAMMETRY

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ABSTRACT

One of the limitations of dynamic electrochemistry, when used as a quantitative analytical technique, is the resolution of overlapping waves. Approaches used in the past have been either time intensive methods using many blanks, or have relied on many empirical peak parameters. Using an approach based on semidifferential voltammetry, two new techniques have been developed for rapid peak deconvolution. The first, NIFIT1, is an iterative stripping routine, while the second, BIMFIT, is based on sequential simplex optimization. Both approaches were characterized by deconvolution of synthetic fused peak systems. Subsequently, both were applied to semidifferentiated linear scan voltammograms of Cd^{2+} , Pb^{2+} and In^{3+} , and to semidifferentiated linear scan anodic stripping voltammograms of Cd^{2+} , In^{3+} and $I\ell^{+}$. Deconvolutions were directly characterized by peak height, peak potential and peak halfwidth, as well as by the total squared deviation of the fit peaks from the real fused peaks. Studies of individual peaks as well as of standard additions to fused peaks showed both

methods worked well, with excellent deconvolution efficiencies.

Synthetic data were totally deconvoluted with peak separation as small as 25 mv, while real systems were deconvoluted with separations below 40 mv. Peak parameters obtained from these deconvolutions allow observations of electrode processes, even in systems containing overlapping peaks.

Introduction

A principal difficulty in the use of dynamic electrochemistry as a quantitative analytical technique is the problem of resolution of overlapping waves. This is of particular importance in linear sweep voltammetry (2.s.v.) and anodic stripping voltammetry (a.s.v.) at a stationary mercury electrode because of the very broad, asymmetric nature of the peaks. Another difficulty is that the current-potential relationship is not describable by an analytic function. These problems are particularly unfortunate since 2.s.v. instrumentation is easy to use and is relatively inexpensive, and compared to most other dynamic electrochemical techniques offers a wide range of scan rates.

There have been up to now two general approaches to electrochemical peak deconvolution: a "hardware" and a "software" approach. The hardware approach is typified by those of Martin and Shain (1) and Bond and Grabaric (2). In both methods a sample is run along with a blank solution containing a suitable background electrolyte and one of the overlapped components. The concentration of this component is varied until upon subtraction of the blank voltammogram from the sample voltammogram (whether by analog or digital means) no trace of the overlapped component is left. Besides being very time intensive, for cases in which the supporting electrolyte is complex the making of a suitable blank may not even be feasible.

The software approach, that of deconvolution after data taking, is perhaps more promising. Annino (3) divided software deconvolution techniques into two types, time domain and frequency domain. Peak resolution in the frequency domain can be accomplished by the method

of Kirmse and Westerburg (4). In this method the Fourier transform of an overlapped spectrum is divided by the transform of a single component, resulting in a sharpened spectrum. In electrochemistry Binkley and Dessey (5) have recently done work on the least-squares fitting of FT transformed square-wave voltammograms. In this procedure the transform of the overlapped peak is fit with the transforms of single peak data in a least squares manner by varying what would be in the time domain the peak height. This procedure is advantageous in that the fit is reduced in complexity by the reduction of points in going to the frequency domain and in that fits may be done on both real and imaginary parts of the transform in order to obtain an averaged, improved fit. The procedure does rely on utilization of empirical single peak parameters, however.

Time domain deconvolution is curve fitting. Curve fitting of electrochemical data has been hampered by the lack of analytic current-potential functions. Some work has been done in this area, principally by Perone and co-workers (6-8). In their most recent paper (8) of this type Boudreau and Perone describe the application of an empirical peak shape function (the sum of skewed gaussian and cauchy functions) in the use of curve fitting in the deconvolution of square wave voltammetric peaks. This function requires five parameters per peak and in addition requires that three "shape" parameters be found from single peak data. The other two parameters are determined from a least squares minimization procedure. Overlapped peaks with separations as small as 30 my are determined.

This paper describes a curve fitting peak deconvolution technique for a stationary hanging mercury drop electrode in which £.s.v. or a.s.v. data, after transformation, are fit with a wave shape function that is derived wholly from theory. Reversible £.s.v. voltammograms are transformed via a technique called semidifferential analysis into a form that is exactly equivalent to a sech² waveform. No empirical single peak parameters are assumed in the curve fitting algorithms, and all fit parameters have a direct physical significance.

Theory

The detailed theory of semiderivative voltammetry has been described elsewhere (9-13). For the application of a linear potential ramp the semiintegral m(E) is defined as (9):

$$m(E) = \pi^{-1/2} \int_{E_i}^{E} \frac{i(\gamma)}{\sqrt{E-\gamma}} d\gamma$$
 (Eqn. 1)

and the semiderivative e(E)

$$e(E) = \frac{\partial m(E)}{\partial E}$$
 (Eqn. 2)

For a reversible charge transfer

$$0x + ne^{-} = Red$$
 (Eqn. 3)

assuming the appropriate boundary conditions the shape of a semiintegral wave is given by (10):

$$E = E_{1/2}^{r} + \frac{RT}{nF} \ln \left[\frac{m^{*} - m(E)}{m(E)} \right]$$
 (Eqn. 4)

where

$$m^* = (D_0 v)^{1/2} nFAC_{0x}^*$$
 (Eqn. 5)

and where D_0 is the diffusion constant of the oxidized species in solution, ν is the scan rate, n is the number of electrons transferred, F is the Faraday constant, A is the surface area of the electrode, and C_{0x}^{\star} is the bulk concentration of the oxidized species. From application of Eqn. 2 to Eqn. 4 the semiderivative is (12):

$$e(E) = \frac{nFm^*}{4RT} \operatorname{sech}^2 \left[\frac{nF}{2RT} (E - E_{1/2}^r) \right]$$
 (Eqn. 6)

The semiderivative is seen to be a symmetric peak with a flat baseline. The height of the peak is linearly proportional to the bulk concentration of oxidized species. At 25°C the peak width at half the peak maximum is (12):

$$W_{p} = \frac{0.0907}{n} V$$
 (Eqn. 7)

For the case of a free metal in equilibrium with N labile metal complexes the semiderivative wave is (9):

$$e(E) = \frac{nFm^*}{4RT} \operatorname{sech}^2 \frac{nF}{2RT} \left\{ (E - E_{1/2}^r) + 1/2 \operatorname{In} \sum_{i=0}^{N} \beta_i [X]^i \right\}$$
 (Eqn. 8)

...

Formation of labile complexes is seen not to affect the shape of either the semiintegral or semiderivative wave but rather moves them to more negative potentials. The treatment of several electroactive species is also straightforward and results in the linear superposition of semiintegral or semiderivative waves (11).

The above equations for £.s.v. also apply to a.s.v. under certain conditions (9), and in addition the condition that no intermetallic compounds be formed within the mercury drop amalgam. The only difference is that the diffusion constant and bulk concentration of oxidized species are taken as those of the reduced species in the mercury drop. Under certain conditions (14) of short plating time, large volume of solution, and reproducible stirring, metal amalgam concentration is proportional to the bulk oxidized species concentration for equal plating times. Under these conditions both semiderivative and semiintegral waves are proportional to oxidized species bulk concentration.

Experimental

Reagents: For the ℓ .s.v. runs stock solutions of Pb²⁺, Cd²⁺, and In³⁺ were made approximately $1.0 \times 10^{-2} \text{M}$. Metallic A.R. Cd and Pb were dissolved in A.R. HNO₃; it was necessary to dissolve 99.95% In₂O₃ in a minimum amount of hot 72% HC ℓ O₄. The solutions were titrated with standard EDTA solution and stock solution concentrations of [Pb²⁺] = $1.96 \times 10^{-2} \text{M}$. [Cd²⁺] = $2.09 \times 10^{-2} \text{M}$ and [In³⁺] = $2.02 \times 10^{-2} \text{M}$ were determined. The supporting electrolyte for these solutions was A.R. HC ℓ diluted to 0.58 M.

For the a.s.v. runs ${\rm Cd}^{2+}$ and ${\rm In}^{3+}$ stock solutions were diluted to $2.09{\rm x}10^{-4}\,{\rm M}$ and $2.02{\rm x}10^{-4}{\rm M}$, respectively, from the stock solutions used in the £.s.v. runs. In addition a ${\rm T£}^{+}$ stock solution was prepared from A.R. ${\rm T£NO3}$, standardized at a concentration of $8.84{\rm x}10^{-3}{\rm M}$, and an a.s.v. stock solution was diluted to $8.84{\rm x}10^{-5}{\rm M}$. The a.s.v. supporting electrolyte consisted of purified HC£ diluted to 0.58 M with water collected from a pre-leached all-vitreous silica still. The HC£ was purified according to the method of Mattison (15) by sub-boiling distillation. Preleached Teflon® bottles were used to contain the purified HC£. All electrochemical cells were carefully cleaned between a.s.v. runs by rinsing with Transistar® grade HNO3.

Cell, Electrodes, and Equipment: The cell and electrodes used in this investigation were the same as those described earlier (9) with the cell thermostatted to $24.9 \pm 0.1^{\circ}\text{C}$ for the l.s.v. experiments and to $23 \pm 1^{\circ}\text{C}$ for the a.s.v. experiments. Equipment used was also described before, with the exception of a solid state relay interfaced with a DAC to control stirring. A Digital Equipment Corporation MINC-11/2B microcomputer was used to control experiments and take data. Another computer with an LSI-11/23 CPU was used for data analysis.

Computer Programs: Control of the L.s.v. and a.s.v. experiments was performed by MACRO-11 assembly language subroutines linked to a FORTRAN driver and other FORTRAN subroutines used for data storage and graphics. Data was stored on disk for later processing. Processing included digital filtering based on fast Fourier transform techniques (16) and semiintegration by a FORTRAN program employing the method of

Huber (17) as given by Nicholson and Olmstead (18). A point by point subtraction program was written to perform a.s.v. background subtraction.

Two different programs were written to deconvolute overlapping peaks. Both fit in a least squares manner experimental semidifferentiated voltammograms with a sum of sech² functions representing the individual components. The first (NIFITI) is an iterative stripping routine similar to a method developed for X-ray spectrometry (19). It is completely self starting except for the number of components to be fit in a semidifferentiated voltammogram and the number of iterations to be performed. On the first cycle the maximum of the semidifferentiated voltammogram is found and is used to define the first peak, and then the peak potential and peak height for this peak. A sech² function is then fit to the side of the peak that is least overlapped by varying the peak width until the sum of the squares of the residuals between calculated and experimental semidifferentiated voltammograms is minimized. The peak made from these three fit parameters is stored in memory and subtracted from the original experimental scan to give a subtracted scan. The process is repeated until calculated peaks for the number of components specified as input are determined.

On the second iteration all but one of the calculated peaks from the first iteration are subtracted from the experimental semi-differentiated voltammogram, resulting in a subtracted semidifferentiated voltammogram of only one peak. The three parameters are then determined from the fit to this peak, and a second order calculated peak is constructed and stored in memory. The process is repeated for the other

peaks until second order peaks have been calculated for all components. The second iteration is then concluded and the program moves to the third iteration. Third order peaks are constructed from second order peaks in the manner just described. The process is concluded when the specified number of iterations have been completed, at which time the final peak potentials, heights, and widths are output.

The second program (BIMFIT) is based on the principle of sequential simplex optimization (20). This program uses the FORTRAN subroutine NELMIN as described by O'Neill (21) based on the algorithm of Nelder and Mead (22). This program takes as input parameters the numeber of peaks, the limiting number of iterations, and the initial guesses of the peak potential, height and width for each peak. The subroutine NELMIN varies all parameters for the fitting function, three for each sech² peak, simultaneously to minimize the squares of the residuals between experimental semidifferentiated voltammograms and the sum of these sech² functions with the aid of a user supplied subroutine to calculate the squares of the residuals. The program stops when the specified number of iterations have been completed.

Procedure: For the £.s.v. single peak studies 25 ml. of 0.58 M HCL was pipetted into the cell and deaerated with Ar for 5-10 minutes to remove dissolved oxygen. After deaeration, a Hg drop was extruded and a voltammogram taken of the supporting electrolyte from -.200 V to -.900 V vs. the Ag/AgCL electrode at a scan rate of 1.0 V/s and written to disk. Then scans were taken of Cd, In, and Pb in different concentrations by adding standard additions of stock solution with an Eppendorf pipette. See Table 1 for a summary

of all solutions studied in this paper.

After all data were taken the voltammograms were digitally filtered, the semiderivative taken and written to disk. Empirically it was found that while the order of filtering and semidifferentiation had no effect on peak potentials, it had a large effect on peak heights. Semiderivative voltammograms obtained by semidifferentiating and then filtering had sloping, non-zero baselines while those made from filtering and then semidifferentiating had flat baselines at nearly zero. The latter case is the result predicted by theory so the order of filtering and then semidifferentiating was used for all voltammograms.

The curve fitting programs NIFIT1 and BIMFIT were then applied to the semiderivative voltammograms with NIFIT1 limited to 10 iterations and BIMFIT limited to 200 iterations. For a semiderivative voltammogram with two peaks, each program required about 15 minutes running time on the LSI-11/23.

The a.s.v. studies were done in the same manner by adding standard additions of freshly made $1.0 \times 10^{-4} M$ stock solutions to 25 ml of deaerated supporting electrolyte. After deaeration, the potential of the h.m.d.e. was changed to -.235 vs. the Ag/AgCl electrode and stirring was instituted to ensure constant flux to the electrode during plating; after 10 seconds the potential was changed to -1.0 V and plating took place for 600 seconds. Six seconds before the end of the plating period stirring was discontinued and the potential changed to -.900 V. This potential was held for 15 seconds to ensure a homogeneous concentration of reduced species within the drop.

Stripping then took place at a scan rate of 1.0 V/s to a final potential of -.200 V.

For each a.s.v. series a scan was first taken of the supporting electrolyte alone to provide a background scan. After all data were taken and digitally filtered the a.s.v. background scans were subtracted point by point from the stripping scans to remove the effects of capacitive current and other background currents (23). The resultant background subtracted voltammograms have the same shape as \(\ell.\s.v.\) voltammograms. Subsequently, semidifferentiation and curve fitting techniques were used on these voltammograms exactly as in the \(\ell.\s.v.\) runs.

Results and Discussion

The programs NIFIT1 and BIMFIT were characterized by deconvoluting synthetic fused peak systems constructed with the ${\rm sech}^2$ curve shape. Table 2 gives the results of the fitting for NIFIT1 limited to ten iterations and for BIMFIT limited to 200 iterations. In Table 2 series A, B, and C show respectively the influence of peak potential, peak height, and peak width on the efficiency of the deconvoluting programs. The variable ${\rm R}^2$ is the coefficient of determination (24) and is

$$R^{2} = 1 - \left\{ \frac{\sum_{i=1}^{N} [Y_{i} - Y(X_{i})]^{2}}{\sum_{i=1}^{N} Y_{i}^{2}} \right\}$$
 (Eqn. 9)

where Y_i is the experimental curve, $Y(X_i)$ is the fit curve, and N= of data points (in all cases=512). Figure 2 shows a synthetic peak and the fit to it along with the deconvoluted components. Results show

that

- 1) for two peaks of equal height and full width at half maximum (FWHM) of 40 mv (approximately the FWHM for a reversible two-electron charge transfer) deconvolution fails only when ΔE_p , the difference between peak potentials, is less than 20 mv
- 2) for peaks of 40 mv FWHM and a 10:1 ratio of peak heights NIFIT1 reproduces initial peak parameters better than BIMFIT, BIMFIT failing at about $\Delta E_p = 30$ mv while NIFIT1 begins to fail at about $\Delta E_p = 20$ mv
- 3) deconvolution efficiency is not reflected solely by 100 R^2 values close to 100. In the B series 100 R^2 values for BIMFIT are all larger than the corresponding NIFIT1 values, yet NIFIT1 much better at reproducing the initial peak parameters
- 4) for a narrow (40 mv FWHM) peak fused with a broad (60-100 mv FWHM) peak NIFIT1 fails appreciably while BIMFIT does well
- 5) both programs return initial peak potentials better than either peak heights or widths.

Real systems:

Parameters obtained for fits to real Cd, Pb, and In £.s.v. single peak systems are shown in Table 3. As seen in 3) above, efficiency of deconvolution should not be judged simply on the basis of $100 \, \text{R}^2$ values close to $100 \, \text{Efficiency}$ should be judged on a combination of good $100 \, \text{R}^2$ values, precision of deconvoluted peak parameters, and consistency between single peak and multiple peak data. In particular, in agreement with Eqns. 5 and 6 straight line fits of deconvoluted peak height vs. concentration for the added component in each series result in R^2 values close to 1, intercepts near zero, and slopes that remain

nearly constant for each component.

Table 4 lists computed values of average peak potentials and widths for all components of each series, average peak heights for components not added, and the slope, intercept, and R² for the straight line fit of concentration to peak height for the added component in each £.s.v. series. In this table and in Table 6, peak parameters for the most dilute component in each series were not included in averages because of the distortion caused by relatively high background noise.

It is seen from Table 3 that NIFIT1 and BIMFIT give nearly identical answers for peak parameters for all systems investigated. Both BIMFIT and NIFIT1 are very good at determining peak potentials in single peak $\ell.s.v.$ systems, standard deviations for BIMFIT being on the order of 0.5 mv and for NIFIT1 on the order of 1 mv. Peak widths for Cd and Pb are near 45 mv, in good agreement with Eqn. 7 for a reversible charge transfer. The peak width of about 35 mv for the In charge transfer is slightly larger than the predicted 30.2 mv for the reversible case, indicating some degree of non-reversibility and a possible deviation from the sech waveform. The 100 R^2 values for the In fits are of the same order as those of the Cd and Pb waveforms, however, indicating that the sech waveform remains a good approximation.

The 100 R^2 values in Table 3 and in nearly all of the series increase monotonically with concentration. The increase is due to the lessening relative importance of noise as concentration is increased. Perone (8) has noted the same effect.

Peak height vs. concentration plots for the single peak l.s.v. systems are shown in Figure 3. All three fits have intercepts near the origin,

as in Eqn. 5. The magnitude of the slope agrees qualitatively with the n^2 dependence of Eqn. 5, as the slope of the indium fit is significantly greater than those of the cadmium or lead fits.

Multiple peak &.s.v.: Table 5 shows the data for the &.s.v. multiple peak systems. Average peak parameters and other information are included in Table 4. A representative peak from the SAL series along with the ${\rm sech}^2$ fit to it and individual components is shown in Figure 4. It is seen that the Pb peak is completely resolved from the In and Cd peaks, which form an overlapped peak system with $\Delta E_{\rm p}$ = 40 mv. Deviations in peak potential are increased over the single peak systems to over one mv, while values of peak potential stay nearly the same as in single peak systems. Peak width values and deviations are nearly the same. Lead peaks show the smallest deviation in peak height, as might be expected for a non-overlapped peak. The indium peaks show the next smallest deviation, while cadmium shows the largest. This is consistent with the supposition that the fit to indium is worse than to the other elements. The fit is to the peak near the peak maximum, while deviation from the sech² waveform would be expected further away from the maximum, and therefore might not be accounted for in the overlap.

Straight line fits of concentration vs. peak height are shown in Fig. 5. The intercepts, in general, are larger than for the single peak system but are still small. The R^2 values are all close to 1, and the slopes of the individual components all agree well with slopes for the single components. The 100 R^2 values are all close to 100.

Single peak a.s.v.: Table 6 shows the results of studies on single peak a.s.v. systems, and the peak averages and the slopes for the straight

line concentration vs. peak height fits are in Table 7. The plot of the straight line fit for the STL series is in Fig. 6. For the single peak systems peak potential determination is very precise, and the indium potential agrees very well with l.s.v. peak potentials. The peak width of about 90 mv for the Tr peak is in good agreement with the 90.7 mv predicted for the theoretical reversible FWHM predicted by Ean. 5 for a one-electron charge transfer. The peak width of 29 mv for indium is also in agreement with a reversible charge transfer, as opposed to the e.s.v. case. The differing chemical environment of the mercury amalgam as opposed to the bulk solution is responsible for the change. The $100~\text{R}^2$ values for the fits are of the same order as the 2.s.v. fits and show the same increase with concentration. The relatively large intercepts in the intercepts of the straight line fits over the &.s.v. case could be due either to the a.s.v. background subtraction or to the effects of larger background noise. The slope of these two lines again agree qualitatively with results expected from Eqn. 5.

Multiple peak a.s.v.: Data for a.s.v. multiple peak systems are shown in Table 8. As in the £.s.v. multiple peak systems deviations in peak potential are increased over the single peak case, but the average potential is nearly unchanged. Peak width values agree well with single peak data in both value and precision.

The straight line fits of concentration to peak height are shown in Fig. 6. Intercepts are again larger than in the £.s.v. case. The slope of the line in the SCD series matches well with the single peak T£ slope. The slopes of the SIN and SALL series are considerably larger, however, though they agree with one another. Fig. 7 shows a peak from

the SIN series and the same peak after the calculated deconvoluted T2 peak was subtracted. The remaining peak is of the right shape for a sech² function for a three electron charge transfer, indicating that the deconvolution process does not account for the increase in peak height. The increase in slope, therefore, does not appear to be due to a flaw in the deconvolution procedure. The increase is possibly due to the formation of intermetallic compounds between thallium and indium in the mercury amalgam. No interaction of these two metals has ever been reported before, but this may be because the overlap of the two peaks makes the system difficult to study. Vydra, et. al. (25) do mention that T2 and In both form intermetallic compounds with mercury.

Although any voltammogram may be semidifferentiated, one disadvantage of the model presented in this paper is that the model applies only to the semiderivatives of reversible charge transfers. For reversible systems, though, the application of the sech² curve fitting procedure to the deconvolution of overlapped l.s.v. and a.s.v. waves is shown to be successful. The procedure results in the direct evaluation of peak parameters useful in thermodynamic, kinetic, and quantitative analyses. In addition it has the advantage of not relying on empirical peak parameters to define the peak shape, so that changes in shape due to charge transfer reversibility or to the occurrence of intermetallic interaction can be noted.

Credit

This work was supported by the U.S. Department of Energy under Contract No. W-7405-ENG-48, and by Contract No. DE ACO6-76RL01830-ONWI between Battelle Memorial Institute and the U.S. Department of Energy.

References

- 1) Martin, K.J.; Shain, I. Anal. Chem. 1958, 30, 1808.
- 2) Bond, A.M.; Grabaric, B.S. Anal. Chem. 1976, 48, 1624.
- 3) Annino, R. Adv. Chromatogr. 1977, 15, 33.
- 4) Kirmse, D.W.; Westerburg, A.W. Anal. Chem. 1971, 43, 1035.
- 5) Binkley, D.P.; Dessey, R.E. Anal. Chem. 1980, 52, 1335.
- 6) Perone, S.P.; Gutknecht, W.F. Anal. Chem. 1970, 42, 906.
- 7) Perone, S.P.; Sybrandt, L.B. Anal. Chem. 1971, 43, 382.
- 8) Boudreau, P.A.; Perone, S.P. Anal. Chem. 1979, 51, 811.
- 9) Toman, J.J.; Corn, R.M.; Brown, S.D. Anal. Chim. Acta, in press.
- 10) Imbeaux, J.C.; Saveant, J.M. J. Electroanal. Chem. 1973, 44, 169.
- 11) Ammar, F.; Saveant, J.M. J. Electroanal. Chem. 1973, 47, 215.
- 12) Goto, M.; Ishii, D.J. Electroanal. Chem. 1977, 77, 225.
- 13) Grenness, M.; Oldham, K.B. Anal. Chem. 1972, 44, 1121.
- 14) Barendrecht, E. "Stripping Voltammetry" in Electroanal. Chem. vol. 2, A.J. Bard, ed., Dekker: New York, 1967.
- 15) Mattison, J.M. Anal. Chem. 1972, 44, 1715.
- 16) Hayes, J.W.; Glover, D.E.; Smith, D.E.; Overton, M.W. Anal. Chem. 1973, 45, 277.
- 17) Huber, A. Monatsh. Math. Phys. 1939, 47, 240.
- 18) Nicholson, R.S.; Olmstead, M.C. in Matlson, J.S.; Mark, H.B.; McDonald, H.C. "Electrochemistry", Dekker: New York, 1972.
- 19) Statham, P.J. Anal. Chem. 1977, 49, 2149.
- 20) Deming, S.N.; Morgan, S.L. Anal. Chem. 1973, 45(3), 278A.
- 21) O'Neill, R. Appl. Statistics 1971, 13, 338.
- 22) Nelder, J.A.; Mead, R. Computer J. 1965, 7, 308.

- 23) Brown, S.D.; Kowalski, B.R. Anal. Chim. Acta 1979, 107, 13.
- 24) F. Mosteller and J.W. Tukey "Data Analysis and Regression",
 Addison Wesley, Reading, Massachusetts, 1977.
- 25) Vydra, F.; Stulik, K.; Julakova, E. "Electrochemical Stripping Analysis", Wiley and Sons Inc.: New York, 1976.

Table I. Composition of solutions used in this work

L.s.v. systems

All 25 ml of 0.58 M HCl background electrolyte with:

Series

SP: 5-20 μ l additions of Pb²⁺ stock solution

SC: 5-20 μ l additions of Cd²⁺ stock solution

SI: 5-20 μ l additions of In $^{3+}$ stock solution

SIC: $100 \, \mu l$ of In^{3+} stock solution and 5-20 μl additions of Cd^{2+} stock solution

SCI: 100 μl of Cd $^{2+}$ stock solution and 5-20 μl additions of \mbox{In}^{3+} stock solution

SPC: 100 μ l of Pb $^{2+}$ stock solution and 5-20 μ l additions of Cd $^{2+}$ stock solution

SAL: 100 μl of both Pb^{2+} and In^{3+} stock solution and 5-20 μl additions of Cd^2+ stock solution

L.s.v. stock solution concentrations:

$$[Pb^{2+}] = 1.96 \times 10^{-2} \text{ M}$$
 $[Cd^{2+}] = 2.09 \times 10^{-2} \text{ M}$ $[In^{3+}] = 2.02 \times 10^{-2} \text{ M}$

A.s.v. systems

STL: 5-20 μ l additions of Tl⁺ stock solution

SINA: $6-20 \mu l$ additions of In^{3+} stock solution

SCD: 50 μ l of Cd²⁺ stock solution and 5-20 μ l additions of Tk⁺ stock solution

SIN: 20 μl of In^{3+} stock solution and 5-20 μl additions of $T\ell^{+}$ stock solution

SALL: 20 μl of both Cd^{2+} and In^{3+} stock solution and 5-20 μl additions of TL+ stock solution

A.s.v. stock solution concentrations:

$$[T_{k}^{+}] = 8.84 \times 10^{-5} \text{ M}$$
 $[I_{n}^{3+}] = 2.02 \times 10^{-4} \text{ M}$ $[Cd^{2+}] = 2.09 \times 10^{-4} \text{ M}$

Table II. Fit peak aparameters for synthetic sech² fused peak systems using programs BIMFIT and NIFITI^a

Series	Potl.b	<u>Height</u> b	<u>Width</u> b	Potl.b	<u>Height</u> b	<u>Width</u> b	100 R ²
AA	35 3500 3502	1.0 1.0026 0.9998	40.0 40.36 40.06	5 5002 4499	1.0 1.0001 0.9988	40.0 39.87 40.06	99.99 99.99
AB	4 3999 3996	1.0 0.9999 0.9981	40.0 40.01 40.06	5 4999 4999	1.0 0.9994 0.9980	40.0 40.00 40.06	99.99 99.99
AC	42 4199 4204	1.0 1.0012 0.9989	40.0 39.91 40.06	5 .4999 4999	1.0 0.9993 0.9987	40.0 40.05 40.06	99.99 99.99
AD	435 4349 4343	1.0 0.9999 0.9994	40.0 40.01 39.88	5 4999 4999	1.0 1.0000 0.9994	40.0 39.99 40.06	99.99 99.97
AE	45 4500 4500	1.0 0.9997 0.9983	40.0 40.35 38.32	5 4999 4994	1.0 0.9960 1.0068	40.0 39.92 40.06	99.99 99.96
AF	46 4597 4598	1.0 0.9928 0.9890	40.0 39.93 36.72	5 4995 4989	1.0 1.0099 1.0302	40.0 39.96 41.38	99.99 99.93
AG	47 4686 4676	1.0 0.9590 0.8529	40.0 38.59 31.48	5 4988 4970	1.0 1.0592 1.1743	40.0 40.38 41.97	99.99 99.72
АН	48 4690 4891	1.0 0.2352 1.6303	40.0 25.63 48.97	5 4919 5048	1.0 1.6459 0.1119	40.0 45.34 20.26	99.96 99.89

a) The first line for each series gives actual input peak parameters. The next two lines give the output parameters for BIMFIT and NIFIT1.

b) Units for potentials are in volts; those for widths in mv; current units are arbitrary.

Table II. (continued)

Series	Potl.b	<u>Height^b</u>	<u>Width</u> b	Potl.b	Height ^b	<u>Width</u> b	100 R ²
ВА	45 4496 4498	0.1 0.0995 0.0984	40.0 39.76 40.06	5 4999 4999	1.0 0.9999 0.9990	40.0 40.15 40.06	99.99 99.99
ВВ	46 4593 4603	0.1 0.0981 0.0999	40.0 39.64 44.07	5 4998 4999	1.0 1.0025 0.9942	40.0 40.09 40.06	99.99 99.99
BC	47 	0.1 0.1378 0.1008	40.0 46.21 44.07	5 5005 5004	1.0 0.9576 0.9895	40.0 39.31 40.06	99.99 99.98
BD	475 4870 4754	0.1 0.2405 0.1032	40.0 46.51 44.07	5 5012 4999	1.0 0.8436 0.9900	40.0 38.91 40.06	99.99 99.99
BE	48 4882 4754	0.1 0.3470 0.0769	40.0 40.13 44.07	5 5026 4992	1.0 0.7911 1.0155	40.0 37.80 40.06	99.99 99.95

Table II. (continued)

Series	Potl.b	<u>Height</u> b	Width ^b	Potl.b	<u>Height</u> b	<u>Width</u> b	100 R ²
CA	45 4500 4500	1.0 0.9961 0.9994	10.0 10.08 10.49	5 5000 4999	1.0 0.9993 0.9988	40.0 39.70 40.06	99.99 99.97
СВ	45 4500 4500	1.0 1.0013 1.0035	20.0 19.77 20.50	5 4998 4999	1.0 1.0024 0.9978	40.0 40.06 39.31	99,99 99,98
CC	45 4500 4500	1.0 1.0001 0.9997	30.0 30.00 30.39	5 5000 4999		40.0 39.98 40.06	99.99 99.99
CD	45 4500 4500	1.0 1.0001 0.9962	50.0 49.97 47.44	5 5000 4994	1.0 1.0003 1.0170	40.0 40.00 41.57	99.99 99.95
CE	45 4500 4495	1.0 1.0002 0.9829	60.0 59.99 55.09	5 5000 4992	1.0 1.0003 1.0481	40.0 39.99 40.06	99.99 99.87
CF	45 4499 4480	1.0 0.9994 0.9614	80.0 79.89 63.41	5 5000 4989	1.0 1.0027 1.1688	40.0 40.05 44.07	99.99 99.42
CG	45 4499 4461	1.0 1.0028 0.9517	90.0 89.29 67.80	5 5001 4989	1.0 0.9985 1.2282	40.0 40.29 44.83	99.99 99.29
СН	45 4495 4441		100.0 99.44 69.45	5 5000 4989		40.0 40.77 46.72	99.99 98.92

Series

701103			6 kJ				U W.		
	Conc.b	Potl.b	<u>Height</u> b	Width ^b	Conc.b	Potl.b	<u>Height</u> b	Width ^b	100 R ²
SP1 ^a	1.57	4784 4791	0.577 0.589	50.7 47.6					80.70 80.43
SP2	3.74	4783 4774	1.105 1.135	47.8 46.4					94.87 94.82
SP3	4.72	4777 4780	1.616 1.619	46.3 45.2					97.19 97.18
SP4	6.29	4781 4789	2.189 2.209	44.6 42.8					98.60 98.33
SP5	7.86	4778 4779	2.684 2.691	46. P					99.00 98.70
SP6	9.42	4776 4775	3.175 3.168	45.0 43.4					99.25 99.06
SC1					1.67	6875 6871	0.426 0.411	34.3 44.1	64.64 61.77
SC2					3.34	6875 6883	0.843 0.812	41.4	91.52 91.36
SC3					5.01	6878 6877	1.354 1.342	41.5 44.1	97.18 96.99
SC4					6.68	6871 6867	1.900 1.859	42.5 44.1	98.64 98.53
SC5					8.36	6872 6879	2.281 2.252	44.3 44.1	99.11 99.10

2

a) The top line of each series gives the BIMFIT results, the bottom the NIFIT1 results b) Units for concentration are 1.0×10^{-5} M , for potential are V vs. the Ag/AgC2 electrode, for peak height are $\mu A/s(1/2)$, and for width are my.

Table III (continued)

Series	terri in 1800 - Million mangan, angiga sana kanapanan jaya mennajar ke Eljanter	iji og skipa – – Skarin – Million – Skarin i Skarin – Gjelov – Teolovic Islausen	In		
	Conc.b	Potl.b	Height ^b	Width ^b	100 R ²
SII	1.62	6513 6492	0.650 0.627	32.0 36.7	86.60 84.89
SI2	3.24	6516 6503	1.342 1.313	33.4 32.6	95.79 95.11
SI3	4.85	6510 6503	1.900 1.878	35.2 35.3	98.07 97.85
SI4	6.47	6511 6503	2.610 2.591	36.1 35.3	98.76 98.48
SI5	8.09	6506 6493	3.352 3.313	35.9 33.4	99.13 98.25

Table IVa: Average peak parameters and results of straight line fits of concentration to peak height for l.s.v. data using BIMFIT

		<u>Cd</u>			In			<u>Pb</u>				_	
Series	Potl.c	Height ^c	Width ^C	Potl.	Height	Width	Potl.	Height	Width	Slope ^{a,b}	Intercept ^{a,b}	$R^{2}a$	
SC	6874± 0.0003		42.4± 1.3							0.285	-0.068	0.9968	
SP							4779± 0.0003		45.9± 1.2	0.333	0.060	0.9996	
SI				6511± 0.0004		35.2± 1.2				0.413	-0.032	0.9979	
SIC	6903± 0.0011		45.7± 1.2	6530± 0.0011	2.426± 0.054	33.4± 0.9				0.286	0.175	0.9978	.
SCI	6915± 0.0012	2.496± 0.122	44.8± 1.4	6520±		33.1± 0.8				0.389	0.170	0.9987	ñ
SPC	6896± 0.0005		42.6± 1.6				4819± 0.0023	2.584± 0.054	45.6± 0.6	0.297	-0.098	0.9959	
SAL	6886± 0.0028		45.0± 1.2	6499± 0.0018	3.317± 0.088	34.5± 0.7	4799± 0.0014	2.697± 0.055	45.7± 1.1	0.279	0.263	0.9954	

a) Slope, intercept and \mathbb{R}^2 refer to the least-squares straight line fit of the concentration of added species in each series to peak height.

b) Units for slope and intercept are $\mu A/[s(1/2)\cdot 1.0E-05\ M]$ and $\mu A/s(1/2)$, respectively. c) Units for potential are V vs. Ag/AgCl electrode, for height are $\mu A/s(1/2)$ for width are mv.

Table IVb: Average peak parameters and results of straight line fits of concentration to peak height for l.s.v. data using NIFITI

		<u>Cd</u>			In			<u>Pb</u>					
Series	Potl.	Height	Width	Potl.	Height	Width	Potl.	Height	Width	Slope	Intercept	<u>R²</u>	
SC	6876± 0.0007		44.1							0.282	-0.082	0.9970	
SP							4779± 0.0006		44.4± 1.4	0.330	0.086	0.9991	
SI				6500± 0.0005		34.2± 1.3				0.411	-0.052	0.9984	
SIC	6901± 0.0015		46.7± 2.4	6526± 0.0010	2.336± 0.102	33.1± 0.8				0.275	0.158	0.9934	
SCI	6915± 0.0013	2.467± 0.107	45.1± 1.6	6518± 0.0016		33.3± 1.5				0.390	0.105	0.9970	2,6
SPC	6896± 0.0005		42.6± 1.6				4819± 0.0023	2.584± 0.054	45.6± 0.6	0.298	-0.126	0.9955	
SAL	6880±		46.3± 1.9	6499± 0.0018	3.317± 0.088	34.5± 0.7	4802± 0.0015	2.704± 0.057	44.9± 1.0	0.273	0.310	0.9963	

Table Va: Fit peak parameters for l.s.v. multiple peak data using BIMFIT^a

<u>Series</u>	Conc. Dot'l Words Widt				<u>In</u>				<u>Pb</u>				
	Conc.	Potl.	Height	Width	Conc.	Potl.	Height	Width_	Conc.	Potl.	Height	Width	100 R ²
SIC1 SIC120 SIC140 SIC160 SIC180 SIC100	1.67 3.34 5.01 6.69 8.36	6868 6891 6917 6901 6902	0.616 1.023 1.585 2.001 2.519	44.1 46.9 44.2 45.5 46.2	8.09 8.09 8.09 8.09 8.09	6550 6535 6529 6530 6522 6517	2.465 2.432 2.390 2.508 2.394 2.365	35.0 32.8 33.2 33.8 33.0 32.5					98.29 98.65 98.87 99.27 99.39 99.53
SCI1 SCI120 SCI140 SCI160 SCI180 SCI100	8.36 8.36 8.36 8.36 8.36	6920 6928 6911 6905 6897 6927	2.301 2.433 2.470 2.534 2.614 2.622	43.2 43.0 44.7 45.7 46.4 45.5	1.62 3.24 4.85 6.47 8.09	6548 6520 6514 6509 6537	0.814 1.453 1.999 2.676 3.347	33.5 32.3 33.3 32.7 34.1					98.93 99.31 99.36 99.46 99.58 99.58
SPC1 SPC120 SPC140 SPC160 SPC180 SPC100	1.67 3.34 5.01 6.69 8.36	6934 6904 6895 6892 6894	0.377 0.884 1.477 1.842 2.385	37.6 40.6 41.9 43.6 44.1					7.86 7.86 7.86 7.86 7.86 7.86	4852 4845 4808 4804 4801 4803	2.679 2.534 2.563 2.605 2.582 2.538	44.7 44.9 46.1 45.9 45.8 46.0	99.06 99.43 99.49 99.52 99.55
SAL11 SAL120 SAL140 SAL160 SAL180 SAL100	1.67 3.34 5.01 6.69 8.36	6847 6873 6875 6867 6928	0.709 1.162 1.739 2.150 2.549	43.6 46.2 45.0 45.2 43.4	8.09 8.09 8.09 8.09 8.09	6504 6489 6492 6489 6485 6532	3.454 3.306 3.315 3.290 3.183 3.354	35.7 34.0 34.4 34.1 33.7 34.9	7.86 7.86 7.86 7.86 7.86 7.86	4797 4797 4794 4791 4790 4827	2.793 2.672 2.726 2.654 2.644 2.690	45.3 46.8 45.5 47.2 44.0 45.6	99.39 99.56 99.57 99.64 99.66

a) For units of parameters see Table III.

Table Vb: Fit peak parameters for l.s.v. multiple peak data using NIFIT1

Series		9	<u>:d</u>			<u>In</u>			<u>Pb</u>					
	Conc.	Potl.	Height	Width	Conc.	Potl.	Height	Width	Conc.	Potl.	Height	Width	100 R ²).
SIC1 SIC120 SIC140 SIC160 SIC180 SIC100	1.67 3.34 5.01 6.69 8.36	6734 6885 6922 6898 6900	0.678 0.991 1.559 1.961 2.492	39.0 50.1 44.7 45.4 46.6	8.09 8.09 8.09 8.09 8.09	6543 6522 6529 6529 6517 6515	2.439 2.181 2.296 2.456 2.347 2.299	33.8 31.9 33.4 34.2 32.8 32.6					97.94 97.51 98.84 99.24 99.27 99.50	
SCI1 SCI120 SCI140 SCI160 SCI180 SCI100	8.36 8.36 8.36 8.36 8.36	6913 6925 6911 6908 6897 6935	2.285 2.417 2.462 2.500 2.569 2.569	42.8 43.8 45.7 46.4 47.1 45.0	1.62 3.24 4.85 6.47 8.09	6541 6514 6514 6504 6541	0.765 1.394 1.921 2.596 3.319	32.8 31.6 33.9 32.6 35.1					98.73 99.31 99.37 99.46 99.50 99.59	
SPC1 SPC120 SPC140 SPC160 SPC180 SPC100	1.67 3.34 5.01 6.69 8.36	6925 6914 6890 6897	0.339 0.867 1.453 1.817 2.543	41.2 39.4 41.6 44.1 44.5					7.86 7.86 7.86 7.86 7.86 7.86	4858 4846 4817 4806 4803 4804	2.679 2.526 2.588 2.609 2.577 2.540	43.2 44.3 43.8 46.1 45.0 45.0	99.03 99.40 99.42 99.50 99.57	28
SAL11 SAL120 SAL140 SAL160 SAL180 SAL100	1.67 3.34 5.01 6.69 8.36	6843 6856 6869 6869	0.747 1.195 1.751 2.138 .2556	45.2 49.0 46.4 45.4 44.5	8.09 8.09 8.09 8.09 8.09 8.09	6490 6486 6486 6486 6527	3.424 3.236 3.186 3.192 3.133 3.253	33.0 33.5 33.8 33.8 34.3	7.86 7.86 7.86 7.86 7.86 7.86	4799 4802 4802 4789 4789 4830	2.796 2.707 2.735 2.634 2.665 2.689	45.2 44.5 43.8 46.6 45.0 44.3	98.79 99.54 99.52 99.62 99.69 99.73	

Table VI: Fit peak parameters for a.s.v. single peak data using programs
BIMFIT AND NIFITIA

<u>Tl</u> <u>In</u>

						-			
<u>Series</u>	Conc.	Potl.	Height	Width	Conc.	Potl.	Height	Width	100 R ²
STLI	0.707	5429	0.0745	96.9					86.13
STL2	1.41		0.1273 0.1287	92.8 84.8					95.10 97.69
STL3	2.12	5435	0.1718	93.3					98.00 97.73
STL4	2.83	5434	0.1749	87.3 91.7					99.25
STL5	3.54	5437	0.2225 0.2769 0.2805	88.1 95.0 84.8					99.11 98.91 98.05
SINAT					1.62	6489 6478	0.541	27.5 24.0	85.97 84.09
SINA2					3.24	6491	1.271	29.8 28.2	97.44 96.39
SINA3					4.85	6482 6493	2.028 1.987	28.8	98.10
SINA4					6.47	6492 6490	2.646	28.6 29.1	97.97 98.73
SINA5					8.09	6482 6489	2.608 3.484	27.8 28.8	97.79 99.07
SINA6					9.70	6482 6489 6482	3.412 4.233 4.150	27.8 28.9 28.1	98.25 99.13 98.36

^aConcentration units are 1.0E-07 M. For other units and table format see Table III.

 $^{^{\}rm b}$ NIFIT1 deconvolution unsuccessful due to low signal.

Table VIIa: Average peak parameters and results of straight line fits of concentration to peak height for a.s.v. data using BIMFIT^a

		<u>Cd</u>			<u>In</u>			T&				0	
Series	Potl.	Height	Width	Potl.	<u>Height'</u>	Width	Potl.	<u>Height</u>	Width	Slope	Intercept	R ²	. Name
STL							5436± 0.0001		93.1± 1.5	0.0706	0.0249	0.9890	
SINA				6490± 0.0002	:	29.1± 0.4				0.4546	-0.2065	0.9990	
SCD	6936 0.0002	± 1.1300± 0.0167	46.5± 0.3				5445± 0.0023		100.0± 1.7	0.0723	0.0310	0.9953	30
SIN				6511± 0.0006	:0.7292± 0.0406	28.4± 0.2	5415± 0.0008		92.8± 0.9	0.0925	-0.0036	0.9975	
SALL	6924± 0.0006	± 0.6139± 0.0104	48.0± 1.2	6497± 0.0005	0.8008± 0.0232	27.5±	5418± 0.0026		88.7± 6.2	0.0980	0.0395	0.9962	

^aAll concentration units are 1.0E-0.7 M, otherwise see Table IVa for explanation of table format and other units.

Table VIIb: Average peak parameters and results of straight line fits of concentration to peak height for a.s.v. data using NIFIT1

		<u>Cd</u>			<u>In</u>			Te				_	
<u>Series</u>	Potl.	Height	Width	Potl.	<u>Height</u>	Width	Potl.	Height	Width	Slope	Intercept	R ²	
STL							5434 [±] 0.0020	=	86.2 [±]	0.0708	0.0263	0.9969	
SINA				0.6484± 0.0004		28.]± 0.3				0.4442	-0.1887	0.9992	
SCD	6936 0.0004	± 1.1322± 0.0168	46.1± 0.2				5434± 0.0012	:	98.5± 2.3	0.0747	0.0243	0.9970	<u>u</u>
SIN					: 0.7149± 0.0408	28.4± 0.2	5440± 0.0017	:	84.9± 6.2	0.0910	0.0035	0.9988	
SALL		± 0.6130± 0.0066	42.5± 0.2		0.8006± 0.0108	29.9± 0.3	5450± 0.0015	:	90.4± 1.2	0.1027	0.0200	0.9995	

Table VIIIa: Fit peak parameters for a.s.v. multiple peak data using BIMFIT

			Cd				<u>In</u>				Tl			
<u>Series</u>	Conc.a	Potl.	Height	Width	Conc.a	Potl.	Height	Width	Conc.a	Potl.	Height	Width	<u>100 R²</u>	-
SCD1 SCD2 SCD3 SCD4 SCD5 SCD6	4.18 4.18 4.18 4.18 4.18	6935 6933 6936 6936 6938 6936	1.136 1.148 1.114 1.149 1.122 1.111	46.6 46.9 46.0 46.3 46.3					0.707 1.41 2.12 2.83 3.54	5474 5419 5446	0.0876 0.1241 0.1875 0.2343 0.2885	94.5 97.5 101.3 100.2 100.9	99.75 99.80 99.69 99.85 99.88 99.92	
SIN1 SIN2 SIN3 SIN4 SIN5 SIN6					1.62 1.62 1.62 1.62 1.62	6510 6509 6507	0.6722 0.6950 0.7272 0.7386 0.7600 0.7819	28.4 28.3 28.2 28.8 28.3 28.5	0.707 1.41 2.12 2.83 3.54	5404 5419 5415	0.0668 0.1244 0.1884 0.2533 0.3300	98.5 93.9 92.8 92.6 91.7	98.34 99.17 99.16 99.45 99.76 99.53	
SALL1 SALL2 SALL3 SALL4 SALL5 SALL5	1.67 1.67 1.67 1.67 1.67	6912 6928 6925 6928 6924 6924	0.6341 0.6084 0.6148 0.6060	47.9 46.0 47.6 49.0 49.3 48.4	1.62 1.62 1.62 1.62 1.62	6498 6498	0.8040 0.7936 0.7598	25.7 28.0 28.6 26.9 27.6 28.3	0.707 1.41 2.12 2.83 3.54	5392 5448 5401	0.1103 0.1835 0.2364 0.3154 0.3916	67.6 80.8 95.1 91.6 87.1	99.67 99.81 99.79 99.75 99.75 99.86	32

a) Concentration units are 1.0E-07 M; all other units are as in Table Va.

Table VIIIb: Fit peak parameters for a.s.v. multiple peak data using NIFIT1

			<u>Cd</u>				In				Tl			
Series	Conc.	Potl.	Height	Width	Conc.	Potl.	Height	Width	Conc.	Potl.	Height	Width	100 R ²	
SCD1 SCD2 SCD3 SCD4 SCD5 SCD6	4.18 4.18 4.18 4.18 4.18	6935 6932 6935 6932 6940	1.1394 1.1517 1.1121 1.1493 1.1202 1.1204	46.4 46.4 46.2 45.9 45.9					0.707 1.41 2.12 2.83 3.54	5374 5421 5449 5428 5437	0.1228 0.1872 0.2334	90.9 101.3 95.8 97.9 99.0	99.75 99.78 99.69 99.81 99.84 99.92	
SIN1 SIN2 SIN3 SIN4 SIN5 SIN6					1.62 1.62 1.62 1.62 1.62	6510 6505 6503 6503	0.6569 0.6785 0.7125 0.7310 0.7479 0.7628	28.2 28.5 28.5 28.2 28.3 28.6	0.707 1.41 2.12 2.83 3.54	5434 5461 5421 5442 5436	0.1291 0.1956 0.2574	78.7 76.0 89.0 85.6 89.0	98.17 98.94 98.82 99.25 99.54 99.42	သ
SALL1 SALL2 SALL3 SALL4 SALL5 SALL5	1.67 1.67 1.67 1.67 1.67	6928 6932 6928 6942 6928 6932	0.6230 0.6164 0.6090 0.6043	42.4 42.6 42.8 42.4 42.6 42.4	1.62 1.62 1.62 1.62 1.62	6503 6503 6517 6503	0.7975 0.8133 0.8002 0.8052 0.7814 0.8058	29.7 29.8 29.6 29.8 30.0 30.3	0.707 1.41 2.12 2.83 3.54	5449 5463 5458	0.2414	73.4 91.8 90.9 89.0 89.9	99.75 99.74 99.74 99.69 99.63 99.78	

Figure Captions

- Figure 1. Fourier transform filtered ℓ .s.v. scan of lead at 9.42×10^{-5} M with the corresponding semiderivative.
- Figure 2. Synthetic fused peak AE with resolved components (See Table 2).
- Figure 3. Peak height vs. concentration plots with corresponding fit straight lines for the single peak £.s.v. systems.

Key to symbols: \square = SP series \triangle = SC series \bot = SI series

- Figure 4. Real semidifferentiated peak with corresponding BIMFIT fit.
- Figure 5. Peak height vs. concentration plots with corresponding straight lines for the multiple peak &s.v. systems.

Figure 6. Peak height vs. concentration plots with corresponding straight line fits for the Tl^{\dagger} a.s.v. single peak and a.s.v. multiple peaks systems.

= SALL series

Key to symbols: \square = STL series \square = SCD series \triangle = SIN series











